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REPORT NO. 55

(10)

FURTHER ASPECTS OF THE STABILITY RELATIONSHIPS OF CONCENTRATED SOLUTIONS OF HYDROGEN PEROXIDE

Prepared for the
Office of Naval Research
Contract Nonr 1841 (11)
NR-092-008

BY
W. C. Schumb

MASSACHUSETTS INSTITUTE OF TECHNOLOGY
Department of Chemical Engineering Cambridge, Mass.

Division of Sponsored Research, Project 7476
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The following account is intended to serve as a summary of some further aspects of studies conducted on the stability relationships of hydrogen peroxide solutions over the period subsequent to October 1957, when an account of stabilization procedures current at that time was presented.*

The interpretation of some of the procedures applied in the stabilization of hydrogen peroxide solutions had been left in an inconclusive state in the earlier account; and for some of these aspects more definitive situations have since been attained.

Among these items may be mentioned the very fundamental question of the relationship of the decomposition rate of hydrogen peroxide solutions to the concentration of the solution, especially in the lower ranges of concentration. Some early experimental evidence had indicated that below about 40 wt. percent H_2O_2 an increasingly sharp rise in the decomposition rate occurred with progressive dilution; other data indicated a nearly constant rate over the entire range of concentration. Furthermore, the effect of added stabilizers upon the rate of decomposition of hydrogen peroxide solutions of varying concentrations was not completely clear.

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* Schumb, W. C., See Report No. 50, prepared for ONR under contract No. 1841 (11); NR-092-008, Feb. 1957. Also see Ind. Eng. Chem., 49, 1759 (1957).

In a careful series of measurements carried out in 1959, the rates of decomposition of hydrogen peroxide solutions were re-determined, starting with an original 90% unstabilized solution. Special attention was given to the range of concentration below 30 wt. percent H_2O_2. The results are shown in the accompanying graph over the range 50-3 wt. percent H_2O_2. These data indicate conclusively that a definite increase in decomposition rate occurs at low concentrations. The rate found for the original 90% solution was about 0.0015 wt. per cent per hr. at 50°C. The lower concentrations were obtained by dilution with specially prepared water, which was distilled directly into the flask containing the hydrogen peroxide solution. The specific conductivity of the water, measured at 25°C, was 8.5×10^{-7} ohm^{-1}.

The decomposition rate of the hydrogen peroxide solutions was found on dilution in this way to remain reasonably constant down to about 10-12 wt. percent H_2O_2; below this point a marked increase was observed, so that at the lowest concentration measured (about 3 wt. percent H_2O_2) the rate had tripled. It is believed that this behavior represents an intrinsic lessening in the stability of these most dilute solutions and is not caused by an accumulation of catalytic impurities introduced in the dilution process.

In an attempt to convert concentrated hydrogen peroxide solutions to more dilute ones without the necessity of adding dilution water, and thus opening the way to possible contamination, the catalytic decomposition on the surface of platinum was resorted to. In one experiment the peroxide solution was smoothly decomposed, so that the concentration fell in 12 days from about 95% H_2O_2 down to about 15%; however, the resulting dilute solution showed a disappointingly large rate of decomposition. It must be assumed that minute particles of platinum -- probably of colloidal dimensions -- are formed, and that their catalytic effect persists even after the platinum foil is withdrawn. This mode of dilution of the concentrated hydrogen peroxide solutions therefore had to be abandoned.

Temperature Coefficient of Decomposition Rate

A common industrial laboratory practice used in estimating the relative stabilities of hydrogen peroxide solutions has been to employ an accelerated decomposition rate test at 100°C over a 24-hour or 48-hour interval. While such a procedure may be considered adequate for rough comparison purposes, it should be pointed out that the uncertainty which still exists in the temperature coefficient of the rate of decomposition of hydrogen peroxide solutions over the interval 50-100°C is such that conversion of the 50°C wt. percent H_2O_2 decomposed per hour

to the 100°C/24 hr. basis may be expected to give only approximate agreement with the observed results at 100°C. Conversion factors variously estimated to lie between 800 and 1200 have been reported.

In a study of the relative effectiveness of inorganic stabilizers such as stannate and sodium pyrophosphate over an extended range of peroxide concentration (20 to 90% H_2O_2), carried out with the purpose of discovering whether some stabilizers are more proficient than others over specific ranges of concentration, determinations were made of the rate of decomposition at 50°C of a commercially available 90% stabilized solution. of hydrogen peroxide, employed as received and known to contain not over 0.5 mg/l. of tin as stannate. The lower concentrations were obtained by dilution of the 90% material with water of high purity. The pH values (taken at tenfold dilution) in all the samples fell between 5.5 and 6.5; no attempt was made to bring them to closer constancy. For comparitive purposes the amounts of sodium stannate tri-hydrate and of sodium pyrophosphate deca-hydrate added to the hydrogen peroxide solutions corresponded to 30 p.p.m. of elementary tin and 30 p.p.m. of $P_2O_7^{4-}$ ion.

The results of these measurements are shown graphically in the accompanying figure (Fig. 2). It will be

seen that the two stabilizers used were adequate to hold the decomposition rate of the peroxide solution at a satisfactorily low value over the entire concentration range studied, with possibly a slight preference for the stannate in the lowest concentrations. The sample of unstabilized hydrogen peroxide, used as received without further purification, showed an increasing decomposition rate on dilution reaching tenfold that of the stabilized samples.

Although these results do not lead us to conclude that stabilizers may be more proficient over some specific ranges of peroxide concentrations than others; and although stannate and pyrophosphate appear to be nearly alike in their protective action in the present case, the sum total of evidence derived from stability studies under various conditions would indicate that stannate is more generally applicable and effective in its protective action than any other single additive.

Considerable attention has been given by various investigators to the question of the compatibility of materials of construction employed in fabricating long-term storage containers for concentrated hydrogen peroxide, such as tanks, drums, etc. Conventionally, aluminum of purity at least 99.6% has been found acceptable for this purpose, although lacking a desirable degree of mechanical strength.

In order to improve the compatibility of the metal with hydrogen peroxide solutions, various conditioning agents have been utilized upon the inner surfaces of the containers, such as concentrated nitric acid or phosphoric acid.

In connection with this subject several series of room temperature tests were carried out over a nine-months' period in order to observe the extent to which corrosion of steel and of aluminum may take place in various concentrations of hydrogen peroxide. In these tests conditioned steel rod and sheet aluminum samples were completely immersed in solutions of hydrogen peroxide of known concentration and allowed to stand at room temperature.

From the results of these tests it may be concluded that the addition of hydrogen peroxide in low concentrations -- from 0.1% to 10% -- inhibits the corrosion and rusting of steel for periods of time which are dependent upon the peroxide concentration. At still higher peroxide concentrations (e.g., 20% H_2O_2) the marked catalytic decomposition of the hydrogen peroxide in the presence of the steel would place a limit upon the inhibiting effect of the peroxide upon the corrosion of the metal.

In the case of the aluminum sheet, corrosion of the metal was apparent in a single day when the lowest

concentration of hydrogen peroxide -- 0.1% H_2O_2 -- was used; but as the percentage of hydrogen peroxide rose, the corrosion lessened, until at 10% H_2O_2 it stopped completely.

Addition of small proportions(such as 0.1 gm. per liter) of a stabilizer such as sodium stannate trihydrate, to the solution was found to contribute to the inhibiting action of the peroxide against corrosion of the steel samples. This effect may have been due, at least in part, to the protective action of the increased pH caused by the addition of stannate.

In all of the aluminum test samples in which hydrogen peroxide and the stabilizer were present, a white precipitate was observed to form after a variable period of time; but not unless both peroxide and stabilizer were employed, leading to the conclusion that hydrolysis of the stannate was involved in the precipitation process.

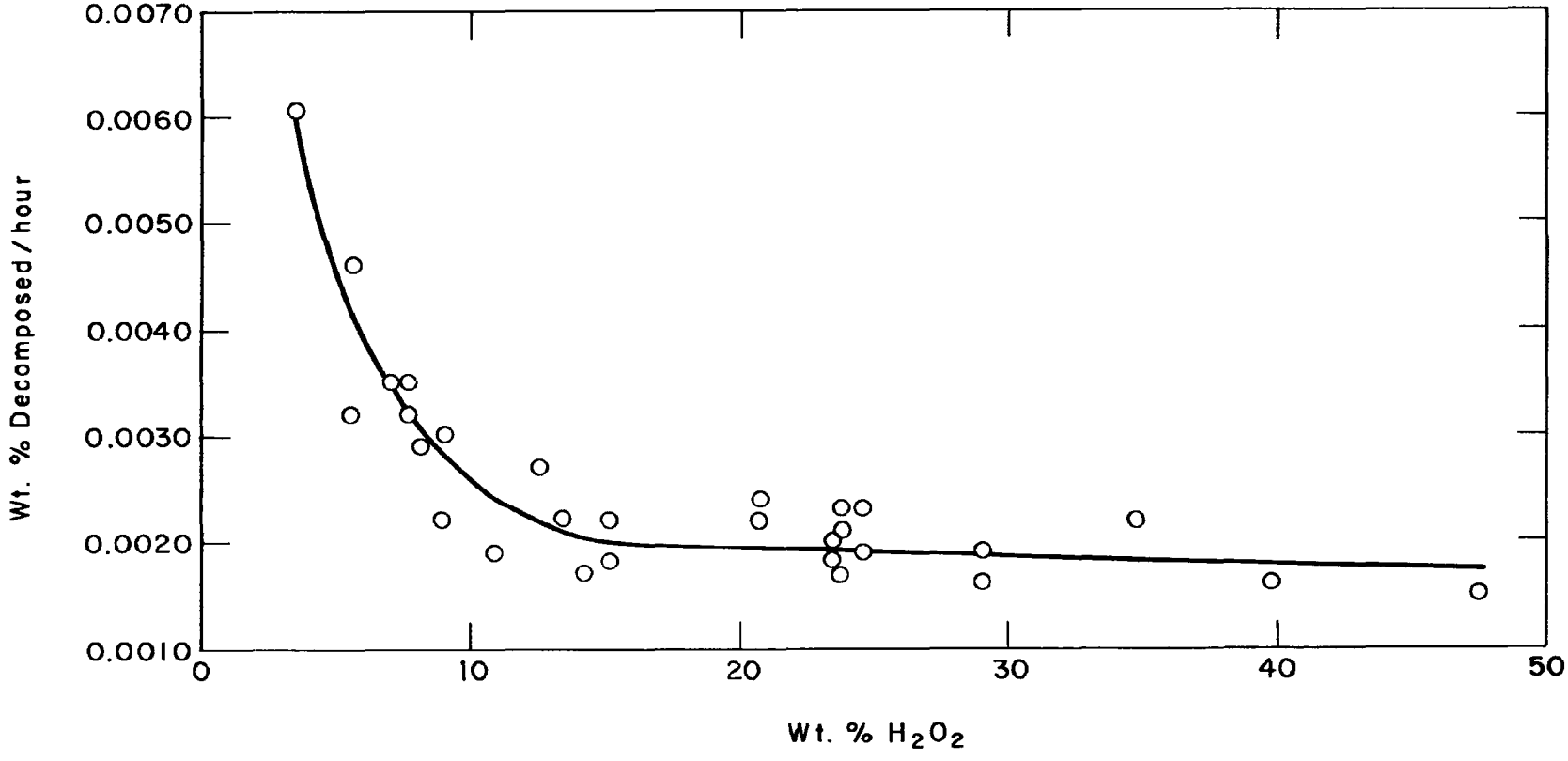

FIG. 1 DECOMPOSITION RATE vs CONCENTRATION OF H_2O_2 50°C

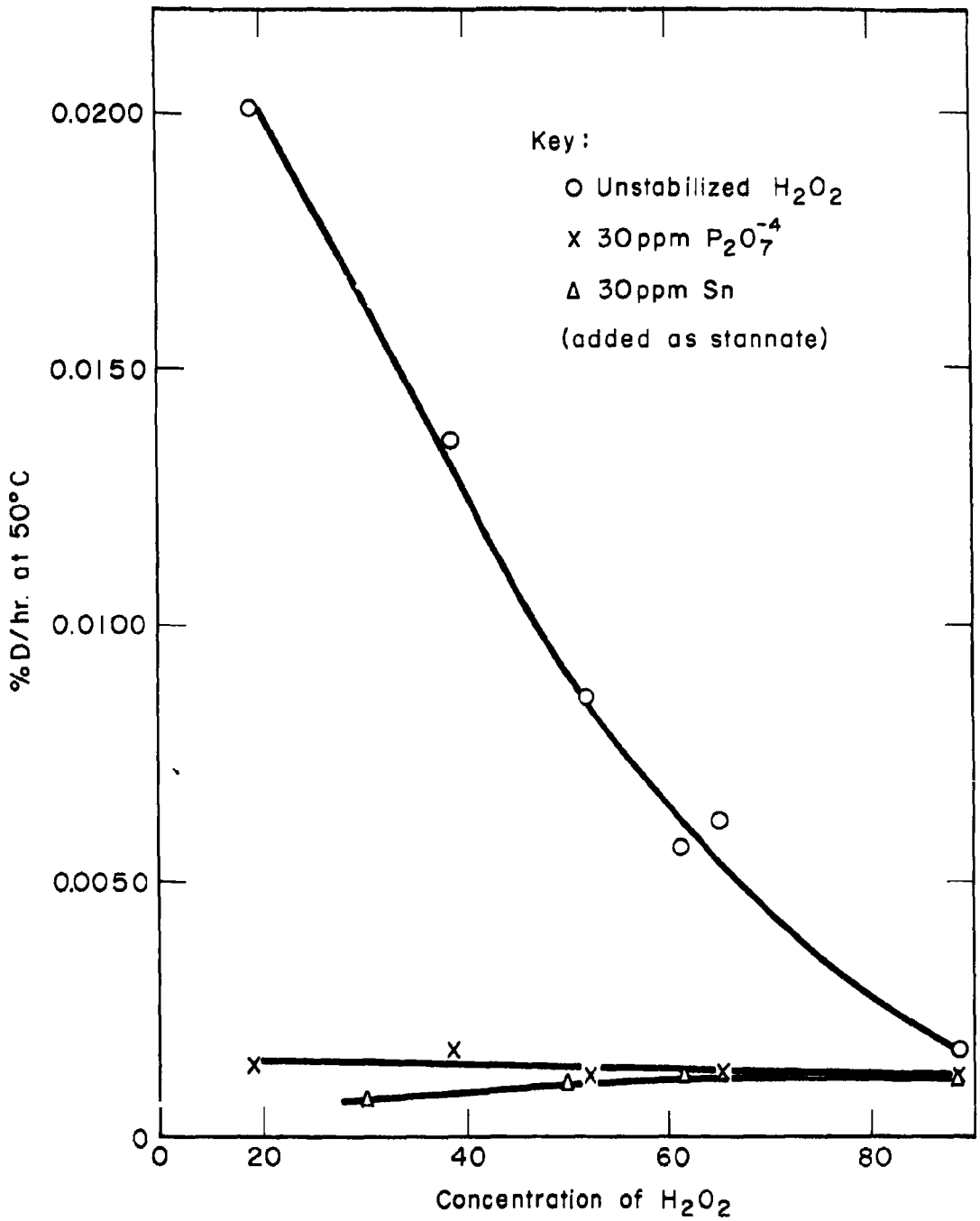

FIG. 2 DECOMPOSITION RATE vs. H_2O_2 CONCENTRATION IN PRESENCE OF DIFFERENT STABILIZERS

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OF HYDROGEN PEROXIDE

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